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Preliminary communication

MECHANISTIC ASPECTS OF PALLADIUM(II) CHLORIDE-CATALYZED CLEAVAGE OF THE Si—Ar BOND. AN UNUSUAL CHARACTER OF SUBSTITUENT EFFECTS

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Summary

The kinetics of the Si—Ar bond cleavages in $Me_3SiC_6H_4X$ (X = H, *m*-Me, *m*-OMe, *m*-Cl, *p*-Me, *p*-Cl) in the presence of Li_2PdCl_4 as the reaction catalyst are first-order with respect both to silane and to $LiPdCl_3L$. In the case of X = *p*-OMe the reaction is second-order with respect to silane and first-order with respect to $LiPdCl_3L$. The reaction is insensitive to substituent effects. A cleavage mechanism is suggested.

Complexes of platinum metals effectively catalyze cleavage of the silicon—carbon bond [1,2]. The mechanism of these reactions has not been studied. We have investigated the kinetics of the Si—Ar bond cleavages in trimethylarylsilanes under the action of Li_2PdCl_4 in 2% aqueous dimethylformamide:

$$Me_3SiC_6H_4X + \frac{1}{2}H_2O \xrightarrow[DMF]{Li_2PdCl_4} \frac{1}{2}Me_3SiOSiMe_3 + C_6H_5X$$

X = H, *m*-Me, *m*-OMe, *m*-Cl, *p*-Me, *p*-OMe, *p*-Cl

Lithium chloropalladate is the reaction catalyst. The turnover number of Li_2PdCl_4 at 100°C exceeds 200 h^{-1}. The reaction of Me_3SiPh with Li_2PdCl_4 in DMF containing 10% of CH_3OD yields 61% of monodeuterobenzene (the expected yield being 91%). This rules out both the free-radical mechanism as the main mechanism of the reaction and the possibility of the palladium salt-catalyzed cleavage of the Si—Ph bond by dimethylformamide.

The rate of the reaction of Me_3SiAr (except Ar = *p*-PhOMe) with Li_2PdCl_4 in DMF at 80—100°C up to 30—50% conversion is described by the first-order equation with respect to silane:

$$w = k_{eff}[Me_3SiAr]$$

Pseudo first-order rate constants are directly proportional to $[Li_2PdCl_4]^{1/2}$:

$$k_{eff} = k' \ [Li_2PdCl_4]^{1/2}$$

$$w = k' \ [Me_3SiAr] \ [Li_2PdCl_4]^{1/2} \qquad (1)$$

We believe that the fractional order with respect to the catalyst is explained by the participation in the reaction of a complex in which the palladium is bonded only to three chlorine atoms, viz. $LiPdCl_3$, or $LiPdCl_3 \cdot DMF$, $LiPdCl_3OH^-$, etc., in equilibrium* with Li_2PdCl_4:

$$PdCl_4^{2-} + L \xrightleftharpoons{K} PdCl_3L^- + Cl^- \qquad (A)$$

When $[PdCl_3L^-] = [Cl^-]$ one has

$$[PdCl_3L^-] = (K \ [PdCl_4^{2-}] \ [L]^{1/2}$$

In the simplest case, when the reaction is controlled by the interaction of Me_3SiAr with $PdCl_3L^-$. the reaction rate should obey the equation

$$w = k \ [Me_3SiAr] \ [PdCl_3L^-] = k \ K^{1/2} \ [Me_3SiAr] \ [PdCl_4^{2-}]^{\frac{1}{2}} \ [L]^{\frac{1}{2}}$$

in agreement with experiment. Introducing LiCl into the solution at constant

TABLE 1

KINETIC DATA FOR THE REACTION OF $Me_3SiC_6H_4X$ WITH Li_2PdCl_4 IN DMF

X	t (°C)	$[Me_3SiC_6H_4X]$ (mol l^{-1})	$[Li_2PdCl_4]$ (mol l^{-1})	$k_{I\ eff}$(×10^5) (sec^{-1})	$k_{II\ eff}$(×10^4) (l mol^{-1} sec^{-1})
H	80	0.15	0.15	1.10 ± 0.02	
	80	0.15	0.075	0.77 ± 0.03	
	80	0.15	0.0375	0.66 ± 0.02	
	80	0.15	0.0075	0.26 ± 0.04	
	80	0.075	0.075	1.07 ± 0.03	
	90	0.15	0.075	1.93 ± 0.03	
	100	0.15	0.075	3.23 ± 0.03	
	100	0.15	0.015	2.20 ± 0.16	
	100	0.075	0.015	2.53 ± 0.11	
	100	0.075	0.075	3.32 ± 0.01	
	100	0.15	0.075^a	2.38 ± 0.05	
	100	0.15	0.075^b	1.57 ± 0.04	
	100	0.15	0.075^c	1.17 ± 0.02	
m-Me	100	0.15	0.075	2.43 ± 0.23	
m-Cl	100	0.15	0.075	2.35 ± 0.10	
m-Meo	100	0.15	0.075	2.15 ± 0.10	
p-Me	100	0.15	0.075	8.33 ± 0.09	
p-Cl	100	0.15	0.075	4.60 ± 0.07	
p-MeO	100	0.15	0.0375		4.23 ± 0.05
		0.15	0.015		2.42 ± 0.15
		0.15	0.0075		1.93 ± 0.07
		0.15	0.15		4.62 ± 0.05
		0.075	0.15		4.48 ± 0.04

a, b, c Experiments with adding LiCl; LiCl in mol l^{-1}: 0.15, 0.375 and 0.75 respectively. Constants are determined by the least-squares method, taking into account statistical weights [10, 11]. Errors are r.m.s. values.

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*Spectrophotometric data of the equilibrium (A) are the subject of a special publication [3].

$[\mathrm{Pd^{II}}]$ leads to retardation of the reaction (Table 1) in accordance with the expected equation

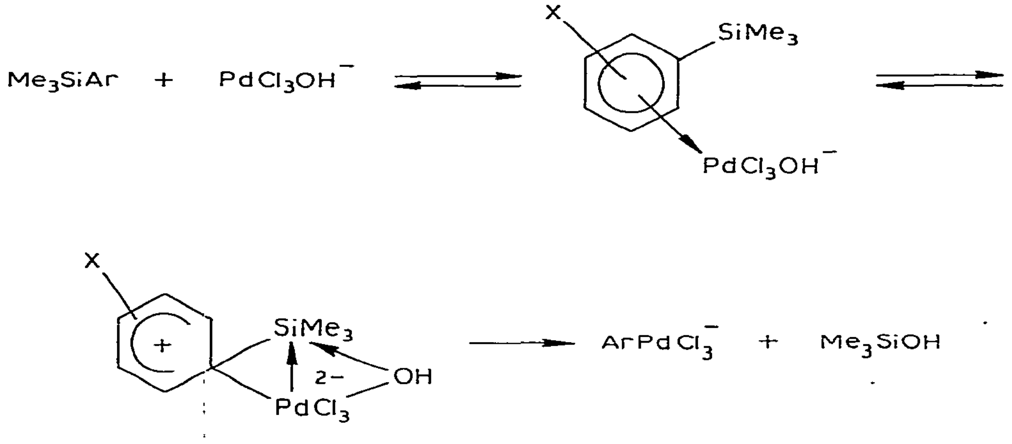
$$k_{\mathrm{eff}} = \frac{k\,K\,[\mathrm{PdCl_4^{2-}}]\,[\mathrm{L}]}{[\mathrm{Cl^-}]}$$

under conditions when $[\mathrm{PdCl_3L^-}] \neq [\mathrm{Cl^-}]$

Unexpectedly it was found that substituents on the aromatic nucleus (*m*-Me, *m*-OMe, *m*-Cl, *p*-Me, *p*-Cl) have a very weak effect on the reaction rate. Silanes of the *m*-series react with practically equal rates irrespective of the nature of the substituent. Substituents in the *p*-position, both donating (Me) and accepting (Cl) somewhat increase the reaction rates ($k_{\mathrm{Me}}/k_{\mathrm{H}} = 2.6$ and $k_{\mathrm{Cl}}/k_{\mathrm{H}} = 1.4$).

As to the character of substituent effects, this reaction differs fundamentally from all known Si—Ar bond cleavages. Thus, in reactions of trimethylarylsilanes with electrophilic reagents (acids, mercury salts, halogens) cleavage rate constants are in a good correlation with σ and σ^+ [4—6] while for reactions with bases these constants are in a good correlation with σ and σ^- at $|\rho| > 1$ [7]. The observed levelling of the substituent effects could be the consequence of the Si—Ar bond cleavage reversibility under the action of the palladium complex. But this appears to be hardly probably. On the other hand, weak substituent effects can be indicative of a very low polarity of the cyclic transition state of the reaction considered. This conclusion is in agreement with the high values of the entropy and enthalpy of activation for the reaction of $\mathrm{Me_3SiPh}$ with $\mathrm{Li_2PdCl_4}$ ($\Delta S^{\neq} = -27.2$ e.u., $\Delta H^{\neq} = 19.4$ kcal/mol at 80—100°C).

The proposed scheme of the reaction includes the formation of a π- and then a σ-complex and its decomposition with the formation of an aryl derivative of Pd. Regeneration of the catalyst proceeds by protodemetallation of $\mathrm{ArPdCl_3^-}$:



$$2\,\mathrm{Me_3SiOH} \longrightarrow \mathrm{Me_3SiOSiMe_3} + \mathrm{H_2O}$$

$$\mathrm{ArPdCl_3^-} + \mathrm{H_2O} \xrightarrow{\mathrm{HCl}} \mathrm{ArH} + \mathrm{PdCl_3OH^-}$$

In contrast to the classical scheme of the Si—Ar bond electrophilic cleavage [4], we propose the palladium atom to be both an electrophile to a carbon atom and a nucleophile with the back-donation to the Si atom. The possibility of a Pd → Si back-donation is discussed in ref. [8]. The electrophilicity of such a palladium atom in the anionic complex is, evidently, not high and the nucleophilic assistance of the OH ligand and its attack on the Si atom are no less important than the electrophilic attack by Pd. Within the framework of this scheme the effect of substituents acting in opposite senses on the electrophilic (C) and on the nucleophilic (Si) centres of the Si—C bond can be small. Indeed, an increase of the nucleophilic assistance in passing from Si to Sn in electrophilic reagents leads to a decrease in the effect of substituents [9].

Introduction of -OMe into the *p* position to $SiMe_3$, in contrast to the above mentioned substituents, leads to a change of the kinetic law. The reaction rate depends on the square but not on the first power of the $Me_3SiC_6H_4$-*p*-OMe concentration:

$$w = k\,[Me_3SiC_6H_4\text{-}p\text{-}OMe]^2\,[Li_2PdCl_4]^{1/2} \qquad (2)$$

The second-order with respect to silane can be explained by the participation in the the limiting step of two silane molecules, one of which forms a π-complex with $LiPdCl_3$. The presence of the Me_3Si group in the *p*-position favours an increase of the relative contribution of the quinoid structure 

and consequently of the π-complex formation with Pd^{II}. In order to satisfy eq. (2), it is necessary, however, that only Pd^{II} complexed with $Me_3SiC_6H_4$-*p*-OMe enters into the reaction with the noncoordinated silane. But this assumption seems to be poorly grounded. The other assumption is the stabilisation of the Pd—C bond in *p*-$MeOC_6H_4PdCl_3^-$, due to electron donation by the OMe group. Thus the protolysis of the Pd—C bond is now much slower than the reaction with the second molecule of the silane, giving the $Ar_2PdCl_2^{2-}$. The protodepalladation of the latter gives the product of the reaction. The data available so far do not allow us to make a choice between the above possibilities.

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